MEMORANDUM

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SUBJECT: MALATHION CONTAMINATION IN THE SPRAY MATERIAL USED FOR MEXICAN FRUIT FLY ERADICATION IN VALLEY CENTER, SAN DIEGO COUNTY

The California Department of Food and Agriculture (CDFA) is using a series of aerial applications of spinosad to eradicate a Mexican fruit fly infestation in San Diego County. The pesticide product used for these applications is GF-120 NF Naturalyte Fruit Fly Bait, containing 200 parts per million (ppm) spinosad by weight as the active ingredient; this product contains no other active ingredients. For application, the GF-120 is diluted with water to a tank mix target concentration of 80 ppm of spinosad. The Department of Pesticide Regulation (DPR) detected 5 ppm of malathion in the tank mixture during the third application and 290 ppm of malathion during the fourth application. A subsequent investigation by DPR and CDFA indicates that a manifold used in the mix/load system is the likely source of contamination. Samples of deposition, water, air, and vegetables collected from the treatment area during and following the fourth application showed no detectable residue of malathion. However, the reliability of the malathion methods used for some of these samples is unknown. CDFA decontaminated or replaced all parts of the mix/load system and aircraft following the fourth application. Samples collected after decontamination showed low or no detectable concentrations of malathion. Samples of the mix/load system and aircraft collected during the fifth application showed no detectable concentrations of organophosphate, carbamate, or chlorinated hydrocarbon pesticides, including malathion.

Background

CDFA is using a series of aerial applications of spinosad to eradicate a Mexican fruit fly infestation in the Valley Center area of San Diego County. The pesticide product used for these applications is GF-120 NF Naturalyte Fruit Fly Bait (U.S. Environmental Protection Agency Registration Number 62719-498), containing 200 ppm (0.020 percent) spinosad by weight (mixture of spinosyn A and spinosyn D) as the active ingredient; this product contains no other active ingredients. For application, the GF-120 is diluted with water to a tank mix target concentration of 80 ppm (0.0080 percent) by weight of spinosad or 0.363 grams per gallon (g/gal). The spinosad target application rate is 3.26 µg/ft^2 (0.142 g/acre, or 35.1 µg/m^2)

DPR is monitoring these treatments to provide information on the amount of spinosad in the spray material and reaching the ground during application, concentrations in air, concentrations in surface water, and concentrations in fruit. DPR has completed monitoring of the first four applications. Preliminary results of the monitoring showed some unusual findings, particularly the detection of malathion in samples collected in the spray material during the third and fourth applications. This memorandum describes the results of samples of the spray material, mix/load system, and aircraft, and an investigation into the source of the malathion contamination.

Description of the Mix/Load and Application Systems

CDFA has modified the mix/load system over the course of the applications. The following is a general description of the mix/load and application systems. Detailed diagrams of the mix/load system used for the first four applications are shown in Figures 1 – 4. The GF-120 used for this project is manufactured by Dow AgroSciences and distributed by Western Farm Service. CDFA personnel constructed the mix/load system primarily using CDFA and rented equipment. The aircraft are owned and operated by Dynamic Aviation Group, Inc., under contract to CDFA.

Western Farm Service and CDFA personnel usually transfer and mix the GF-120 with water the day before the scheduled application. Western Farm Service delivers the GF-120 in 55-gallon drums to CDFA's mix/load site at French Valley Airport near Temecula. At the mix/load site, Western Farm Service transfers the GF-120 from 44, 55-gallon drums into one or more 4,000-gallon storage tanks (Tanks 1 – 3, Figures 1 – 4). At the time of transfer, Tanks 1 and 2 each contain approximately 2,000 gallons of water. The GF-120 is then transferred into Tanks 1 and 2 either directly from the 55-gallon drums or from Tank 3. Western Farm Service rinses the 55-gallon drums with water and places the rinsate into a ball tank. CDFA uses the rinsate in the ball tank for the subsequent application. After the GF-120 is placed into Tanks 1 and 2, CDFA adds additional water from a fire hydrant. Applications 1 – 4 each used approximately 2,350 gallons of GF-120 and 3,500 gallons of water, split between Tanks 1 and 2.

During the application, CDFA personnel transfer the GF-120/water mixture from Tanks 1 and 2 into three fixed-wing aircraft through a series of valves, pumps, meters, and other equipment. The three aircraft each contain a tank that holds the 240 gallons used for each load. Each aircraft uses approximately eight loads for each application. The spray material is applied through five nozzles attached to a boom under the wings. At the end of application, the mix/load system and aircraft spray system are rinsed with water. Rinsate from the mix/load system is placed in Tank 2 and used for the subsequent application. The rinsate from the aircraft are placed in a vat and then transferred to Tank 2 and used for the subsequent application.

Description of Sampling and Analysis for Malathion Contamination

DPR staff collected samples from the spray material, mix/load system, and aircraft to determine the source of malathion contamination. Four types of samples were collected: GF-120, GF-120/water mixture, rinsate, and water. The GF-120 and GF-120/water mixture samples were collected from the material in the 55-gallon drums and Tanks 1, 2, and 3. Rinsate samples were collected from the mix/load equipment and aircraft. Water samples were collected from the hydrant. Additional water samples were collected from the mix/load system and aircraft after decontamination. All samples were collected in new brown plastic or amber glass bottles. The samples were kept refrigerated until laboratory analysis.

The CDFA Center for Analytical Chemistry analyzed all samples. Two different methods were used to analyze the samples, one for the GF-120 and GF-120/water mixture samples, and one for the rinsate and water samples. Both methods used gas chromatographs with mass selective detectors for analysis. The GF-120 and GF-120/water mixture samples had a detection limit of approximately 5 ppm for malathion. The rinsate and water samples had a detection limit of approximately 0.0001 ppm for malathion. The difference in detection limits was due to the smaller aliquots and higher concentration of interferences with the GF-120 and GF-120/water mixture analysis.

Dow AgroSciences split several of the DPR samples. In addition, they sampled archived GF-120 spray material. All samples were analyzed for malathion by Dow AgroSciences' laboratory in Indianapolis.

Results of Samples From the Mix/Load System

During the First Four Applications

Monitoring results from the mix/load system for the first application are shown in Figure 1. During the first application, DPR collected samples of the GF-120 from the 55-gallon drums, and the GF-120/water mixture from Tank 1. The GF-120 contained 208 ppm of spinosad, close to the expected concentration of 200 ppm. The first application occurred over two nights. During the first night (January 7, 2003), Tank 1 contained 202 ppm of spinosad, much higher than the expected concentration of 80 ppm. The high concentration was likely due to insufficient mixing of Tank 1. During the second night (January 9, 2003), Tank 1 contained 90 ppm, closer to the expected concentration. None of the samples contained detectable concentrations of organophosphate, carbamate, or chlorinated hydrocarbon pesticides.

Results from the second application on January 21, 2003 are shown in Figure 2. Tank 1 contained 78 ppm of spinosad. No other samples of the mix/load system were collected. No organophosphate, carbamate, or chlorinated hydrocarbon pesticides were detected.
Results from the third application on February 4, 2003 are shown in Figure 3. CDFA made several changes in the mix/load system between the second and third applications. CDFA moved the mix/load site from an area near the tarmac to one of the hangars at French Valley Airport. In addition, a filter and a loading manifold were added to the system. DPR collected a sample of Tank 1 from the output at the end of the loading manifold. This sample contained 96 ppm of spinosad and 5 ppm of malathion, a common insecticide. The laboratory unequivocally identified the malathion using a mass selective detector. DPR received the results of the third application on February 20, 2003.

Results from the fourth application on February 18, 2003 are shown in Figure 4. CDFA made a minor modification in the mix/load system for the fourth application. The GF-120 was transferred directly from the 55-gallon drums into Tanks 1 and 2. For the prior applications, the GF-120 was first transferred into Tank 3. As with the third application, DPR collected a sample of Tank 1 from the loading manifold. Because of the unusual results from the third application, DPR expedited the analysis of the sample for the fourth application, and received the results on February 26, 2003. This sample contained 80 ppm of spinosad and 290 ppm of malathion. The laboratory unequivocally identified the malathion using a mass selective detector. A second chemist and instrument confirmed the malathion detection.

None of the equipment in the mix/load system or aircraft was used for any other pesticide applications since the start of this program. Therefore, DPR and CDFA initiated an investigation into the cause and potential impact of the malathion contamination.

Malathion Concentrations in Environmental Samples

From the Fourth Application

For the fourth application, DPR collected its normal environmental samples of deposition, water, air, and fruit for spinosad. To determine the potential impact of the malathion contamination, DPR directed the laboratory to attempt to analyze some of the spinosad samples for malathion. None of the 26 deposition samples contained detectable concentrations of malathion. However, these samples were optimized to detect spinosad. The reliability of these samples to detect malathion is unknown. Environmental samples from the third application were not analyzed because the concentrations would have been far below the malathion detection limit.

On February 27, 2003, DPR also collected two lettuce samples and one cabbage sample from organic farms in the treatment area specifically for malathion. No malathion was detected.

However, the treatment area received several inches of rain between the fourth application and the date of this sampling.

Results of Samples From the Mix/Load System and Aircraft

Before and After Decontamination

Between February 28, 2003 and March 3, 2003, CDFA decontaminated or replaced all parts of the mix/load system and aircraft. DPR collected additional samples before and after decontamination to determine the source of contamination and to ensure the systems were sufficiently cleaned. GF-120 or GF-120/water mixture remaining after the fourth application was sampled from the 55-gallon drums, and Tanks 1 and 2. The leftover GF-120 from the third application remaining in Tank 3 was also sampled. The remaining samples of the mix/load system consisted of rinsates of the equipment. Except the vat, all of the equipment had been previously rinsed after the fourth application; therefore, these samples consisted of a second rinse. The vat contained the original rinsate from the fourth application.

Results of the samples collected prior to decontamination are shown in Figure 5 and Table 1. Forty-three of the 55-gallon drums and Tanks 1, 2, and 3, containing the leftover GF-120 or GF-120/water mixture contained no detectable malathion, with a detection limit of approximately 5 ppm. Only 43 of the 44 drums used for the fourth application could be located. Tanks 1 and 2 contained leftover material from the fourth application, as well as approximately 2,000 gallons of water, in preparation for the fifth application, but the tanks had not been mixed. The samples from Tanks 1 and 2 contained 20 ppm and 33 ppm of spinosad, respectively. If Tanks 1 and 2 originally contained 80 ppm of spinosad and 290 ppm of malathion during the fourth application on February 18, 2003 and the proportion stayed consistent, the expected concentration of malathion at the time of sampling on February 28, 2003 was 70 – 120 ppm, well above the 5 ppm detection limit.

Several rinsates from the remaining parts of the mix/load system and the aircraft contained detectable concentrations of malathion (Figure 5 and Table 1). The highest malathion concentrations were detected in samples from the loading manifold and the vat containing the aircraft rinsate. The sample from the vat is the only one containing the original rinsate from the fourth application.

Samples of rinsates from the mix/load system and aircraft after decontamination showed low or no detectable concentrations of malathion (Figure 6). Rinsate samples from two of the aircraft showed higher malathion concentrations after decontamination than before. Samples collected after decontamination may have inadvertently contained malathion from the surface of the spray booms or nozzles. Additionally, the rinse water was transferred from aircraft to aircraft in series, in which cross contamination between the aircraft may have occurred. Tank 2 had no detectable malathion before contamination, but 0.0001 ppm of malathion after decontamination. This is likely due to differences in detection limit. The GF-120/water mixture analyzed before decontamination had a detection limit of approximately 5 ppm. The rinsate from Tank 2 after decontamination had detection limit of approximately 0.0001 ppm

Dow AgroSciences did not detect malathion in any of the archived GF-120 product lots, with a detection limit of approximately 1 ppm.

Results of Samples From the Mix/Load System and Aircraft

During the Fifth Application

Results from the fifth application on March 5, 2003 are shown in Figures 7 and 8. CDFA made a minor modification in the mix/load system for the fifth application. Rinsate from the 55-gallon drums of the fourth application was not used for the fifth application. Before the fifth application, a composite sample from each of the four lots of GF-120 was collected and analyzed. During the fifth application, DPR collected GF-120/water mixture samples from Tanks 1 and 2, the loading manifold, and the three aircraft. Spinosad concentrations ranged from 78 to 98 ppm. No organophosphate, carbamate, or chlorinated hydrocarbon pesticides, including malathion were detected in any of the samples.

Discussion and Conclusions

Malathion was unequivocally identified in several samples collected from the mix/load system and the aircraft. It's likely that malathion was applied during the third and fourth applications because malathion was detected in samples from the aircraft nozzles before and after decontamination, as well as in the aircraft rinsate from the fourth application. The level of malathion contamination may be high relative to the amount of spinosad, particularly during the fourth application where the malathion concentration exceeded the spinosad concentration. However, the 290 ppm of malathion detected in the sample from the fourth application may not be representative of the entire 5800 gallons of spray mixture applied because malathion was not detected in the leftover spray material of Tanks 1 and 2.

Even if the all of the spray mixture from the fourth application contained 290 ppm of malathion, the impacts were likely negligible. Malathion was not detected in any of the environmental samples from the fourth application, although the environmental samples may not be reliable for malathion. Malathion is a common pesticide, and has been used for fruit fly eradication programs on several occasions. The malathion used for fruit fly eradications is normally applied at a rate of 950 $\mu g/ft^2$. If the spray mixture contained 290 ppm of malathion, the application rate would have been approximately 12 $\mu g/ft^2$, or one to two percent of the normal rate. DPR has monitored previous fruit fly eradication programs using malathion (Ando, et al. 1996; Bradley, et al. 1997; Segawa, et al. 1991). A risk assessment conducted by the Office of Environmental Health Hazard Assessment concluded that the aerial application of malathion posed no significant risk to public health at the normal application rate of 950 $\mu g/ft^2$ (Russell, et al., 1991).

From the available information, the source of contamination is not clear. There are five possible sources of contamination: the GF-120 product, the water, the mix/load system, the aircraft, or sampling/laboratory analysis.

The GF-120 product is an unlikely source of the contamination, but it cannot be completely eliminated. Malathion was not detected in any of the archived GF-120 lots used for the third or fourth applications. Analysis of 43 of 44 drums used for the fourth application did not detect malathion. Unfortunately, the last drum could not be located, so the GF-120 cannot be completely eliminated as a source of contamination.

The water used in the mix/load system is an unlikely source of contamination. The mix/load system uses water from a fire hydrant. Malathion was not detected in samples of the water from the hydrant. Malathion would need to occur intermittently in the water hydrant for it to be the source of contamination.

The mix/load system is a likely source of contamination, but there are inconsistencies in the information. This is a likely source of contamination because the original samples containing malathion from the third and fourth applications were collected from the loading manifold of the mix/load system. Samples from the loading manifold had one of the highest malathion concentrations in comparison to the other samples. The loading manifold and filter were first used for the third application, and the loading manifold was first sampled during the third application.

There are two main inconsistencies with the loading manifold as the source of contamination. First, malathion was detected in parts of the mix/load system "upstream" of the loading manifold. However, it is possible for a small amount of backflow to occur in the system. It is also possible that malathion contamination from the third application was recycled through the entire mix/load system via the aircraft rinsate. The second inconsistency is that the sample from the fourth application had a much higher malathion concentration (290 ppm) than the third application (5 ppm). If the manifold was the source of malathion, one would expect dilution to reduce the malathion concentration from the third to the fourth application since the loading manifold was not used for anything else between the third and fourth application.

Other parts of the mix/load system are less likely sources of contamination, although there are several vulnerable points for contamination. The other parts of the mix/load system had lower malathion concentrations compared to the loading manifold. Tanks 1 and 2 are among the most vulnerable points for contamination. However, if Tanks 1 and 2 were the source of contamination, the samples collected just before decontamination should have contained 70 – 120 ppm malathion. Since no malathion was detected, either the tanks did not contain malathion or the malathion degraded during the 10-day period between samples. Malathion degrades rapidly under alkaline conditions (pH >7), but the material in Tanks 1 and 2 were slightly acidic (pH 4). The ball tank is another vulnerable point of contamination. It contained the rinsate from the drums of the third application, but this sample also had no detectable malathion.

The aircraft are a possible, but less likely source of contamination. Samples from the nozzles of all three aircraft had detectable malathion concentrations. In addition, the vat containing the rinsate from the aircraft had the highest malathion concentration. The vat had the highest concentration probably because it is the one piece of the system that still contained the original rinsate from the fourth application. These results are consistent with the loading manifold as the source of contamination. In order for the aircraft to be the source of contamination, significant backflow in the mix/load system would need to occur. The backflow would need to contaminate the loading manifold on a continuous basis, since this was the point of the original sampling for the third and fourth applications.

Errors in the sampling or laboratory analysis are a possible, but less likely source of contamination. All materials used for the sampling were new, used once, and discarded. Each sample was collected with new disposable gloves. The laboratory analyzed quality control samples concurrently with the field samples, including blanks. None of the blanks contained malathion. If the contamination was due to sampling or laboratory errors, it's likely that either all samples would contain malathion, or the malathion would be detected randomly. Most parts of the system have been sampled more than once. The same parts are consistently positive or negative for malathion. The DPR staff assigned and materials used for this project have not been used to monitor malathion applications for several years.

Future Activities

DPR and CDFA will expand its monitoring of the mix/load system and aircraft for future applications. DPR or CDFA will collect samples and analyze samples of each lot of GF-120 prior to its use. DPR or CDFA will collect samples of the mix/load system and aircraft for each application.

References

Ando, C., R. Gallavan, P. Wofford, A. Bradley, D. Kim, P. Lee, and J. Troiano. 1996. Environmental Monitoring Results of the Mediterranean Fruit Fly Eradication Program, Riverside County 1994. Report EH 95-02. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, California.

Bradley, A., P. Wofford, R. Gallavan, P. Lee and J. Troiano. 1997. Environmental Monitoring Results of the Mediterranean Fruit Fly Eradication Program, Ventura County, 1994-1995. Report EH 97-05. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, California.

Russell, H., S. Book, R. Jackson, A. Fan, M. DiBartolomeis. 1991. Health Risk Assessment of Aerial Application of Malathion Bait. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Sacramento, California.

Segawa, R.T., J.A. Sitts, J.H. White, S.J. Marade, and S.J. Powell. 1991. Environmental monitoring of malathion aerial applications used to eradicate Mediterranean fruit flies in Southern California, 1990. Report EH 91-03. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, California.

Attachment

bcc: Segawa Surname File

Table 1. Results of sampling after the fourth application, prior to decontamination. See Figure 5 for a diagram of the sample locations.

Sample Location	Sample Type	Malathion (ppm)	Approximate Detection Limit (ppm)
55-gallon Drums*	GF-120	ND**	5
Ball Tank	GF-120 Rinsate (3rd applic)	ND	0.0001
Transfer Pump	2nd Rinsate	ND	0.0001
Hydrant	Water	ND	0.0001
Mixing Pump	2nd Rinsate	ND	0.0001
Tank 1	GF-120/Water Mix	ND	5
Tank 2	GF-120/Water Mix	ND	5
Tank 3	GF-120 (3rd applic)	ND	5
Loading Pump	2nd Rinsate	0.0023	0.0001
Filter	2nd Rinsate	0.0007	0.0001
Flow Meter	2nd Rinsate	~0.01	0.0001
Loading Manifold	2nd Rinsate	1.4	0.0001
Nozzles of N7198Y	2nd Rinsate	0.027	0.0001
Nozzles of N70U	2nd Rinsate	ND	0.0001
Nozzles of N7136M	2nd Rinsate	ND	0.0001
Vat	1st Rinsate	2.3	0.0001

*GF-120 from 43 of the 44 55-gallon drums were analyzed. The last drum could not be located.
** None Detected

Table 2. Results of sampling after the fourth application, after decontamination. See Figure 6 for a diagram of the sample locations.

Sample Location	Sample Type	Malathion (ppm)	Approximate Detection Limit (ppm)
Transfer Pump	Water	ND*	0.0001
Tank 1	Water	ND	0.0001
Tank 2	Water	0.0001	0.0001
Filter	---	Not Sampled**	---
Loading Manifold	---	Not Sampled	---
Nozzles of N7198Y	Water	0.017	0.0001
Nozzles of N70U	Water	0.0003	0.0001
Nozzles of N7136M	Water	0.0061	0.0001

* None Detected
**A new filter and loading manifold were installed.

Figure 1
Mexican Fruit Fly Spinosad Mix/Load System
Monitoring Results During Application 1 (1/7/03 and 1/9/03)

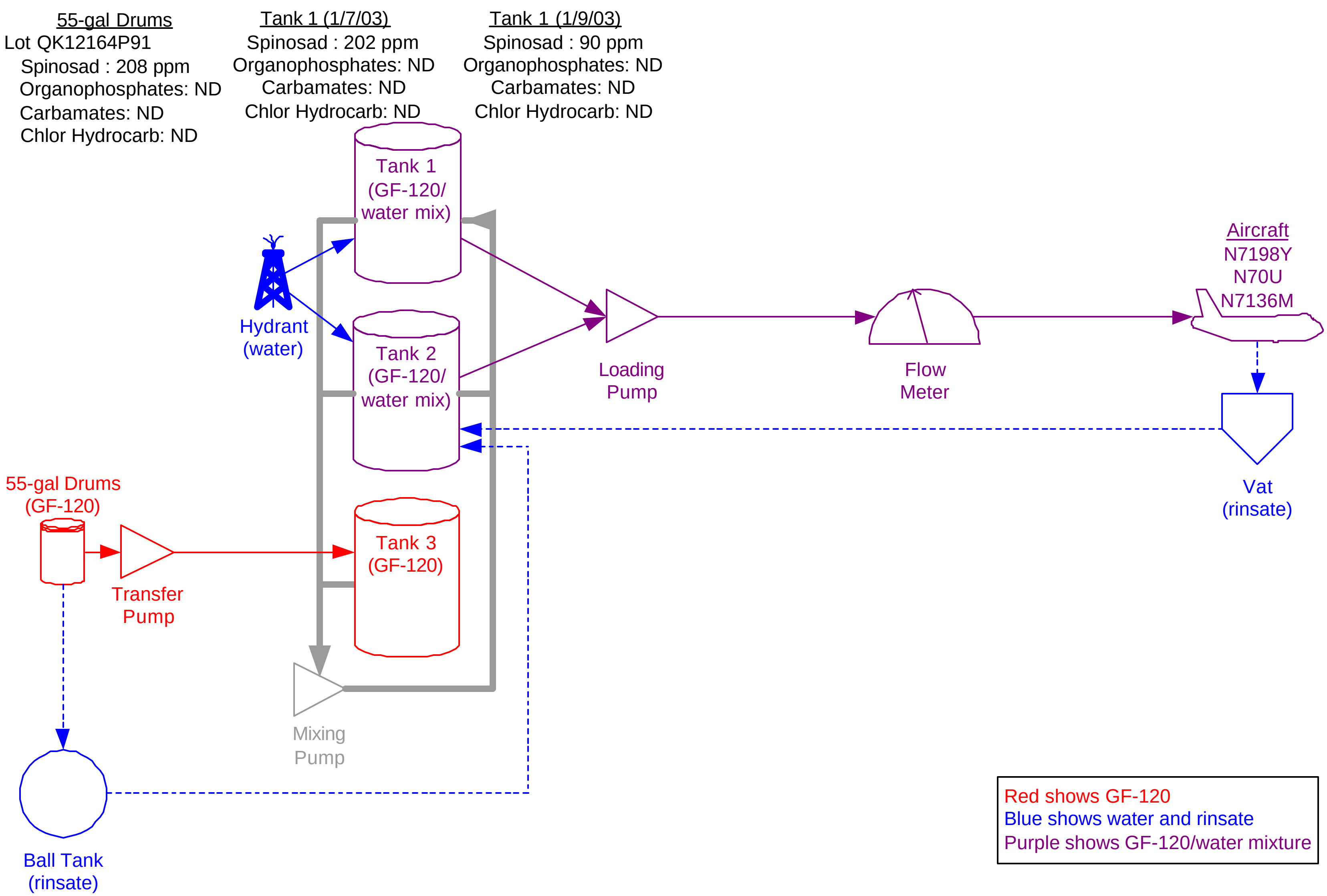


Figure 2
Mexican Fruit Fly Spinosad Mix/Load System
Monitoring Results During Application 2 (1/21/03)

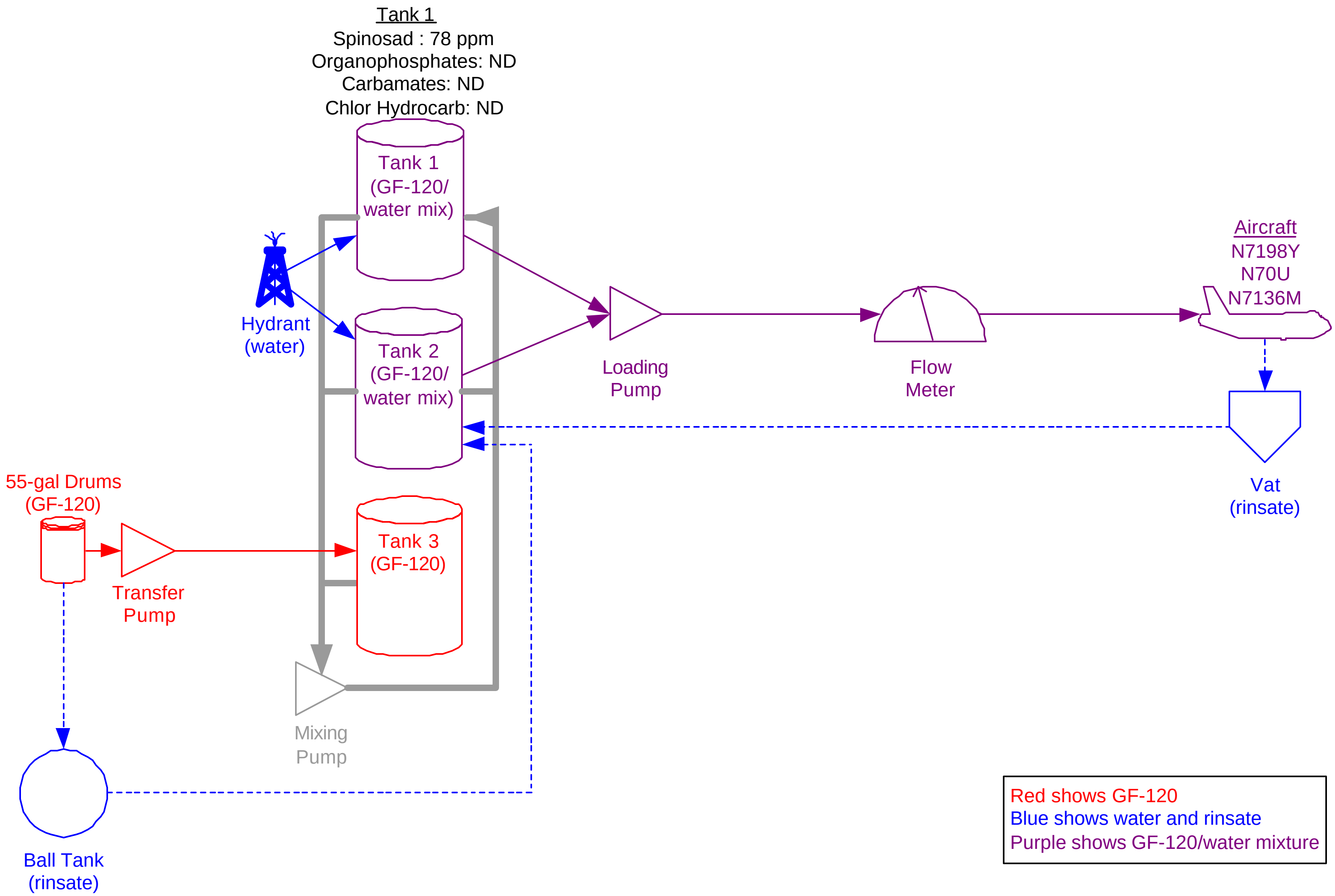


Figure 3
Mexican Fruit Fly Spinosad Mix/Load System
Monitoring Results During Application 3 (2/4/03)

Loading Manifold (Tank 1)
Spinosad : 96 ppm
Malathion: 5 ppm (5,000 ppb)
Carbamates: ND
Chlor Hydrocarb: ND

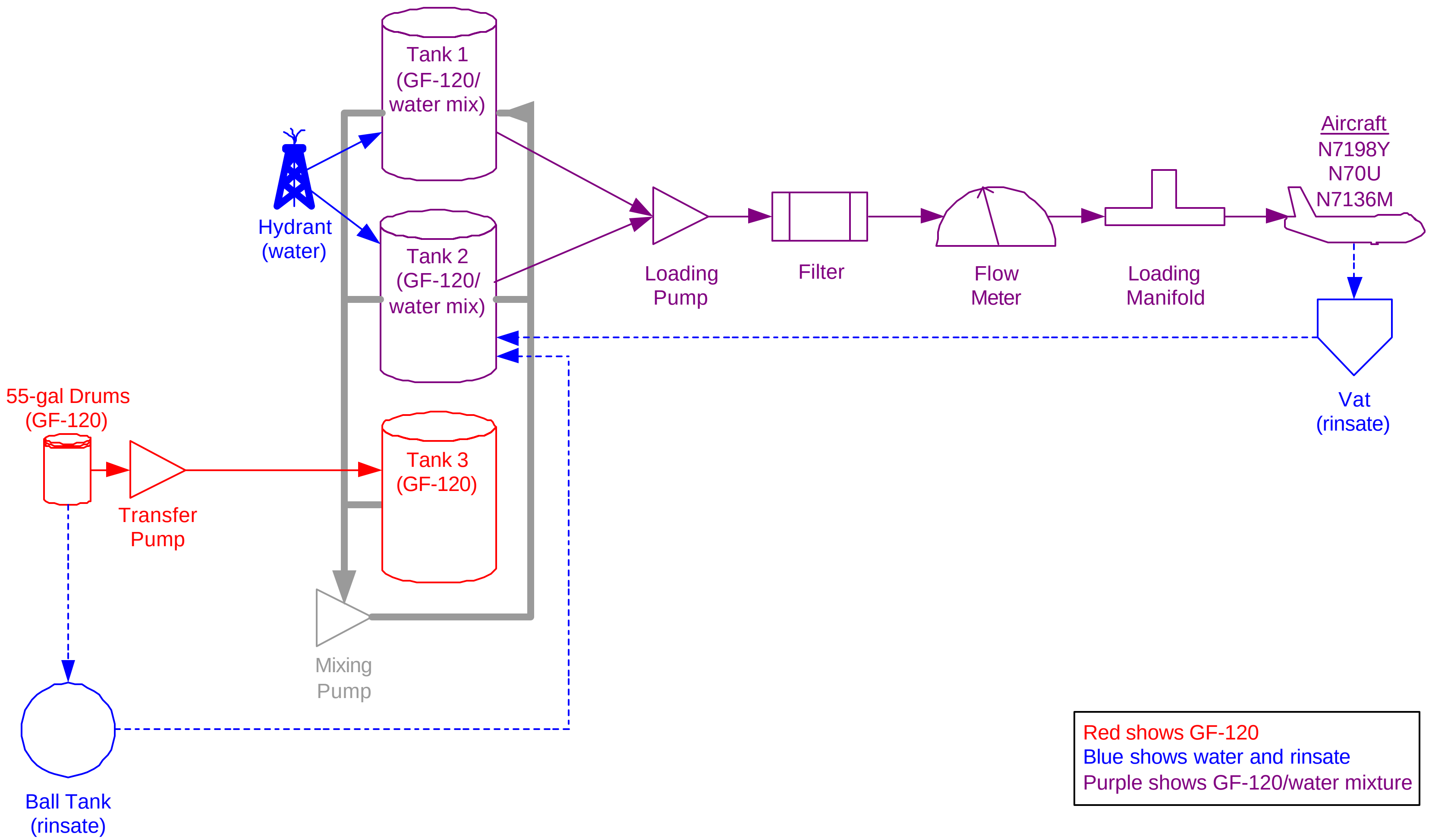


Figure 4

Mexican Fruit Fly Spinosad Mix/Load System

Monitoring Results During Application 4 (2/18/03)

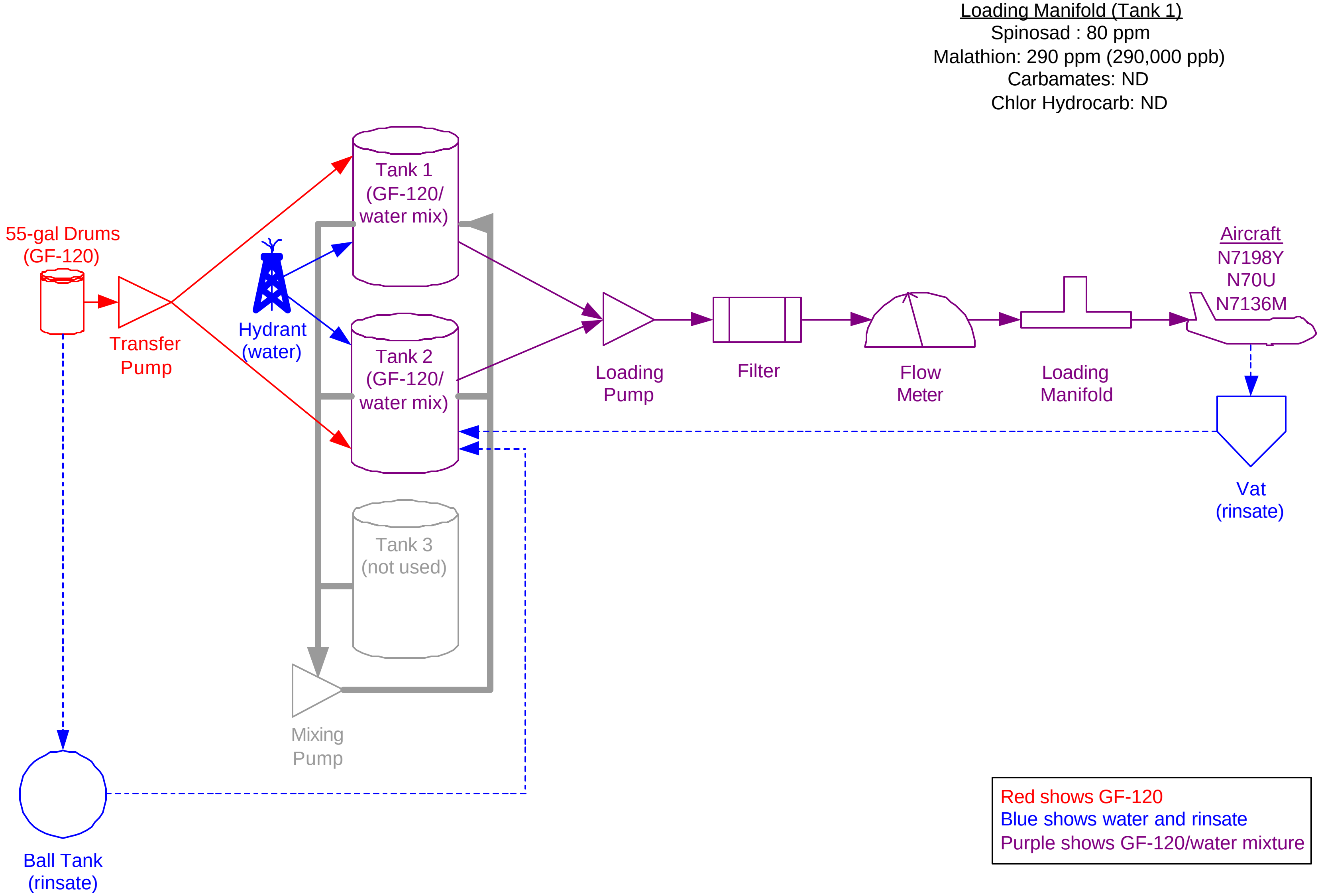
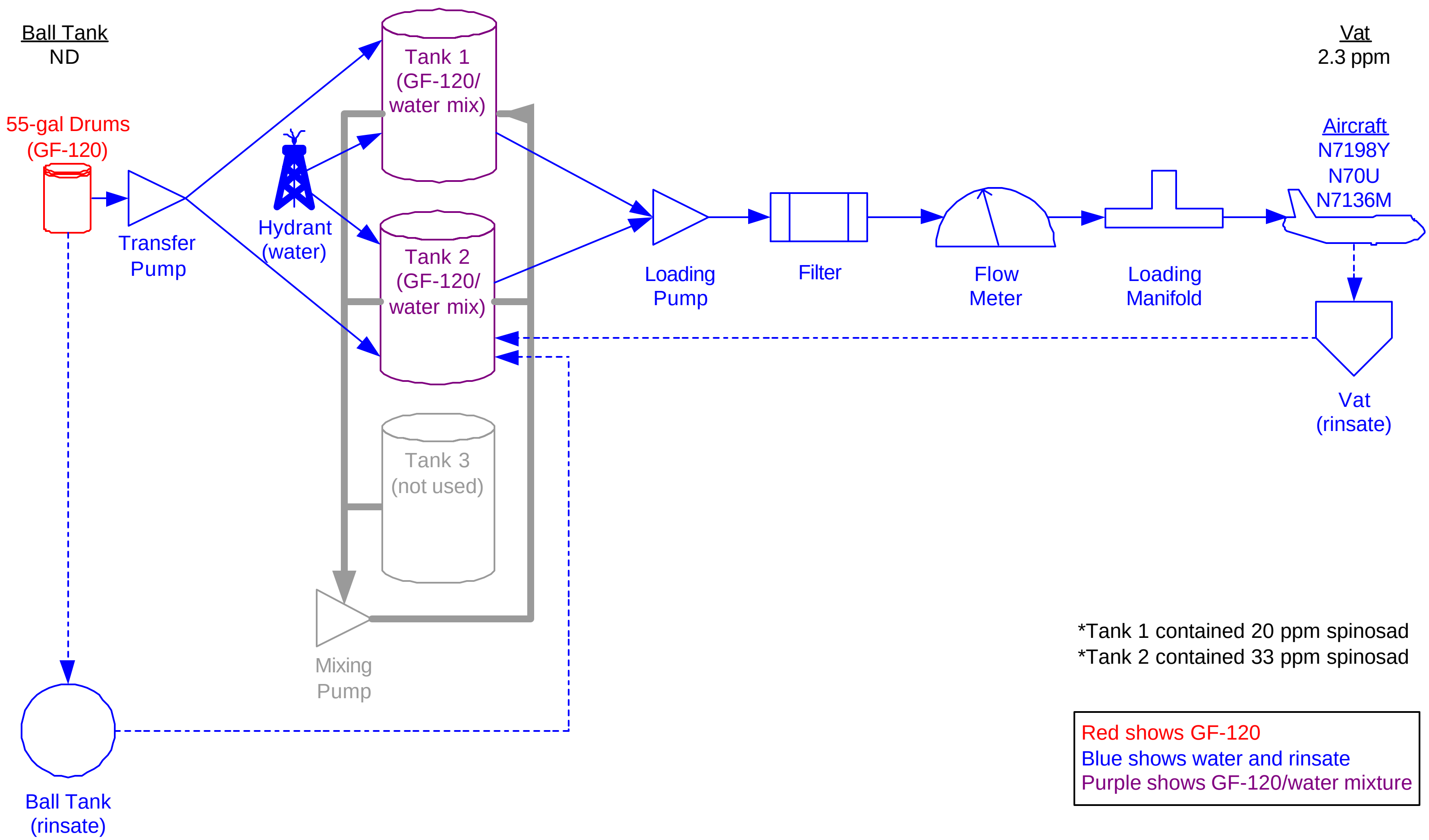


Figure 5
Mexican Fruit Fly Spinosad Mix/Load System
Malathion Monitoring Results After Application 4; Prior to Decontamination (2/27/03 - 3/1/03)

55-gal Drums	Transfer Pump	Hydrant	Mixing Pump	Tanks*	Loading Pump	Filter	Flow Meter	Loading Manifold	Aircraft Nozzles
43 of 44 drums ND	ND	ND	ND	Tank 1: ND Tank 2: ND Tank 3: ND	0.0023 ppm	0.0007 ppm	~0.0100 ppm	1.4 ppm	N7198Y: 0.027 ppm N70U: ND N7136M: ND

Ball Tank
ND

Vat
2.3 ppm



*Tank 1 contained 20 ppm spinosad
*Tank 2 contained 33 ppm spinosad

Figure 6
Mexican Fruit Fly Spinosad Mix/Load System
Malathion Monitoring Results After Decontamination (3/1/03)

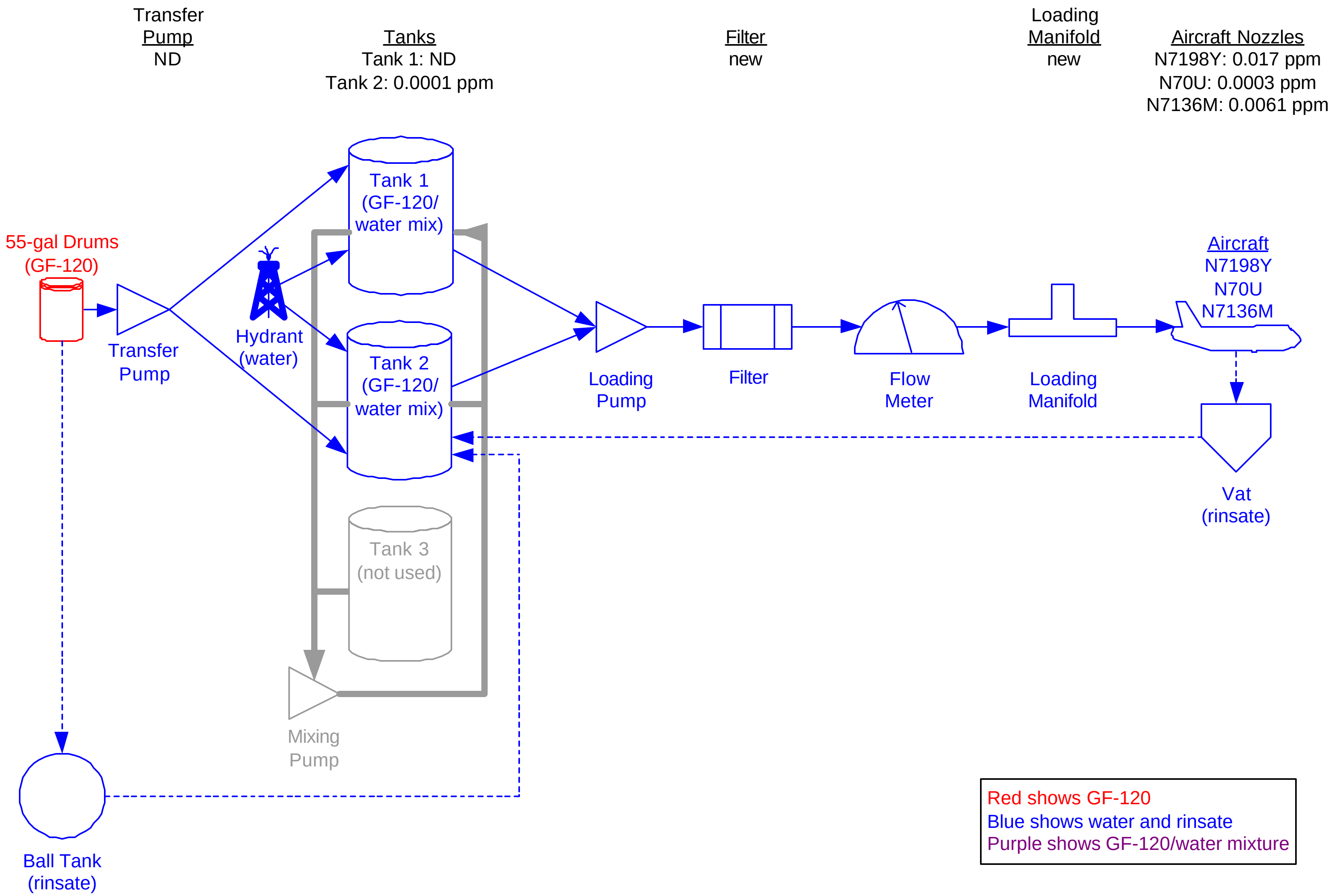


Figure 7
Mexican Fruit Fly Spinosad Mix/Load System
Monitoring Results for Organophosphates, Carbamates, and Chlorinated Hydrocarbons
Prior to Application 5 (2/28/03)

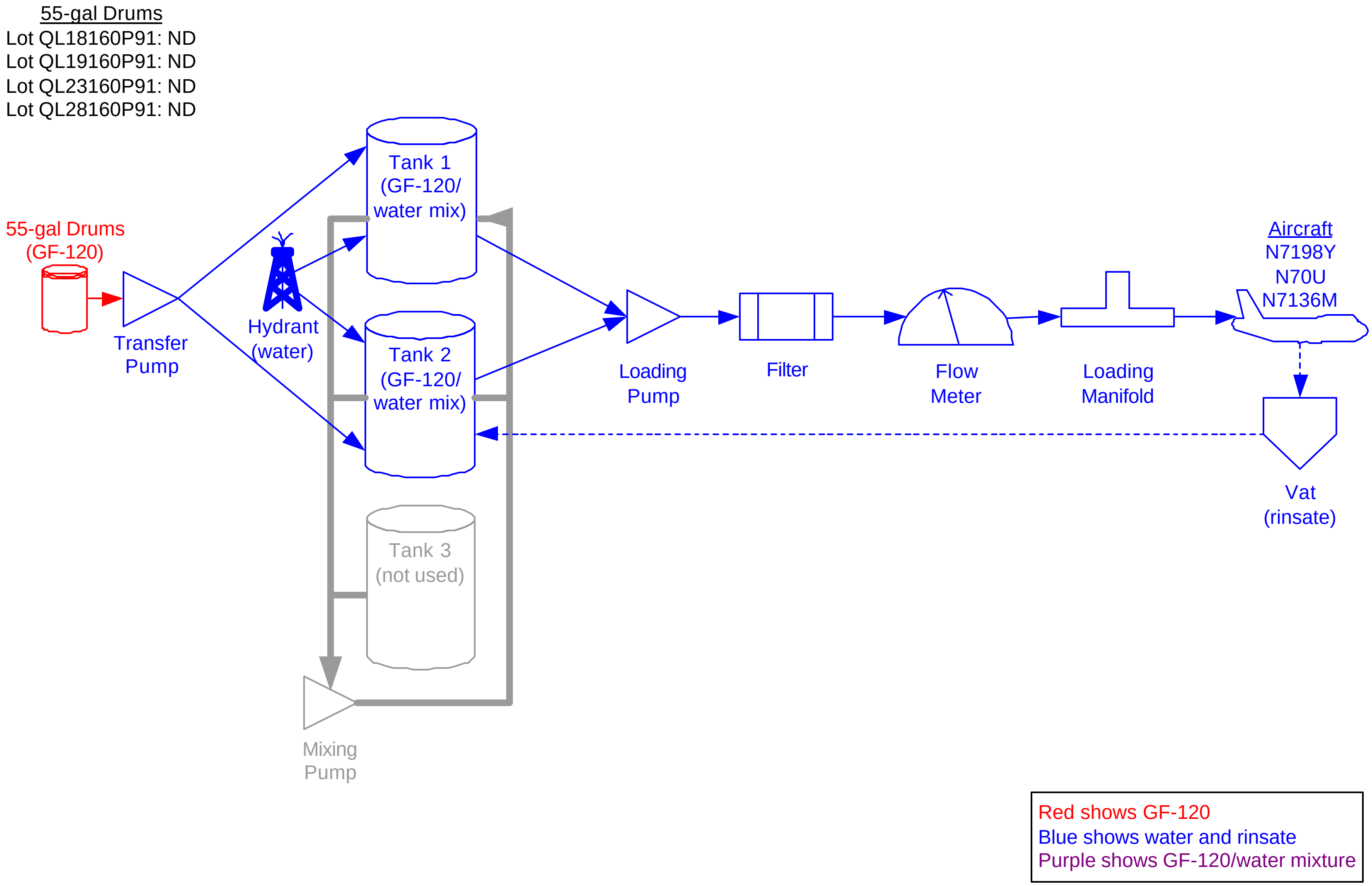


Figure 8
Mexican Fruit Fly Spinosad Mix/Load System
Monitoring Results for Spinosad During Application 5 (3/5/03)

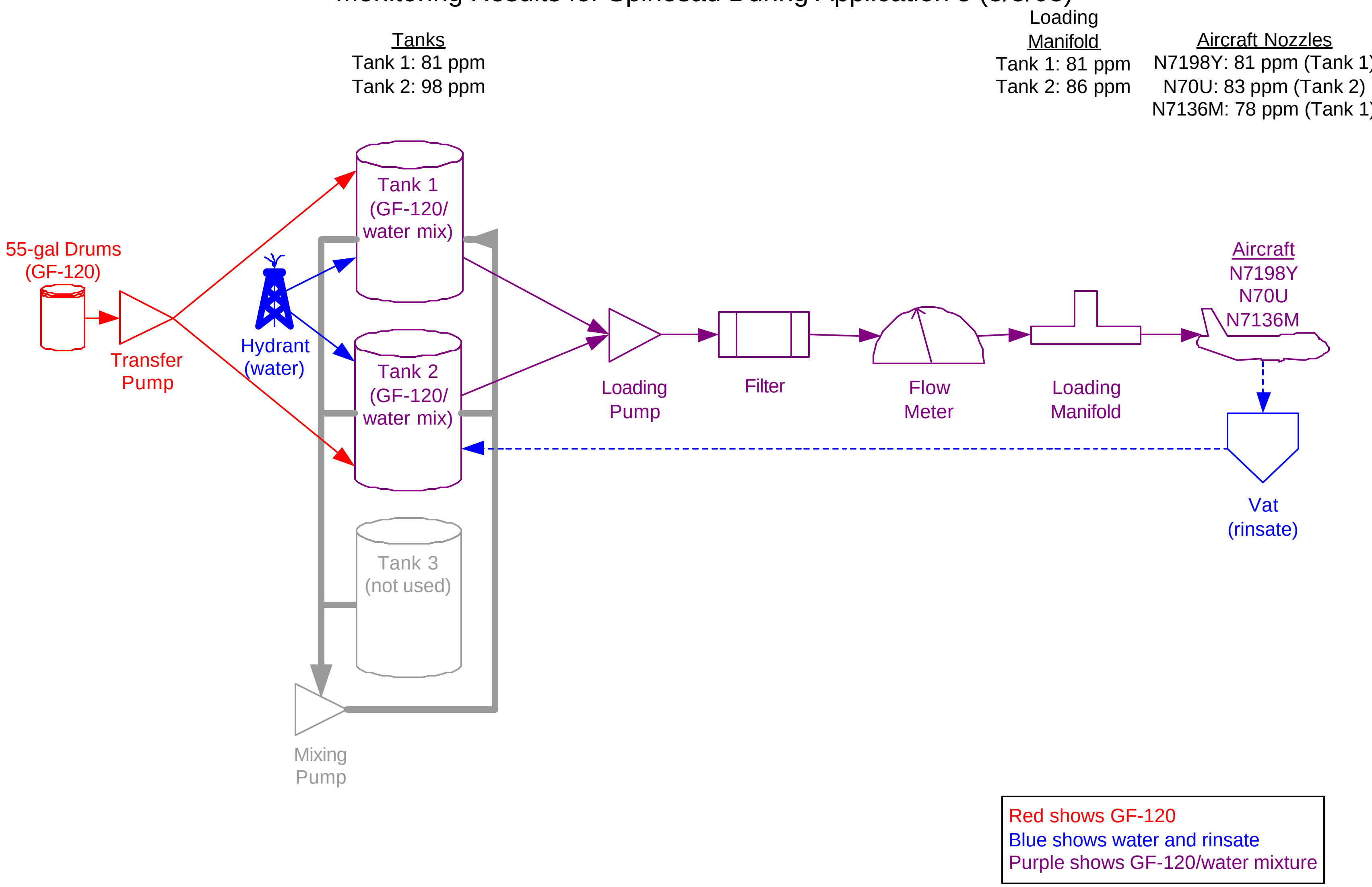


Figure 9
Mexican Fruit Fly Spinosad Mix/Load System
Monitoring Results for Organophosphates, Carbamates, and Chlorinated Hydrocarbons During Application 5 (3/5/03)